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(54) **ELECTROCHEMICAL CO-PRODUCTION OF CHEMICALS WITH SULFUR-BASED REACTANT FEEDS TO ANODE**

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(58) **Field of Classification Search**

None

See application file for complete search history.

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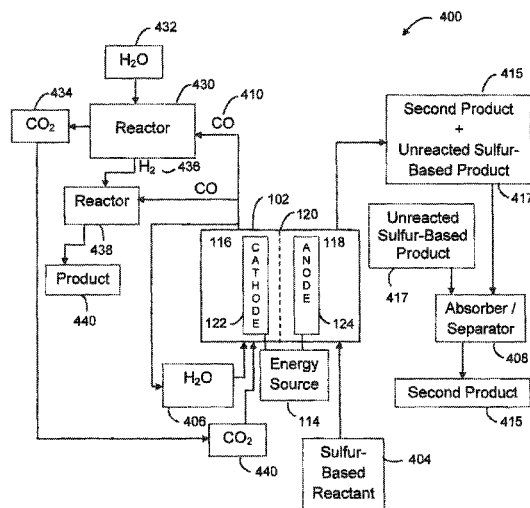
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(57) **ABSTRACT**

The present disclosure includes a system and method for producing a first product from a first region of an electrochemical cell having a cathode and a second product from a second region of the electrochemical cell having an anode. The method may include a step of contacting the first region with a catholyte comprising carbon dioxide. The method may include another step of contacting the second region with an anolyte comprising a sulfur-based reactant. Further, the method may include a step of applying an electrical potential between the anode and the cathode sufficient to produce a first product recoverable from the first region and a second product recoverable from the second region. An additional step of the method may include removing the second product and an unreacted sulfur-based reactant from the second region and recycling the unreacted sulfur-based reactant to the second region.

33 Claims, 12 Drawing Sheets



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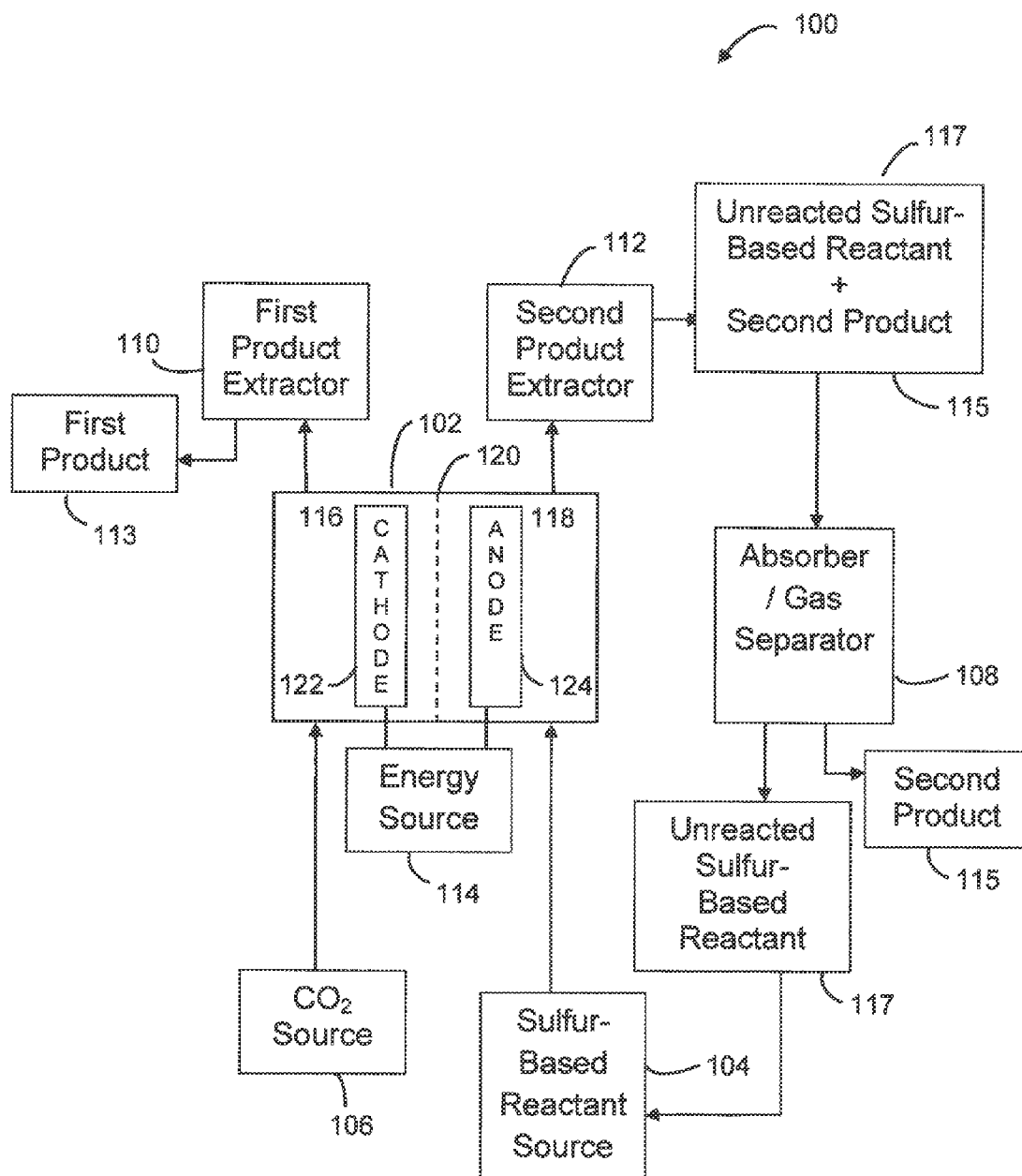


FIG. 1A

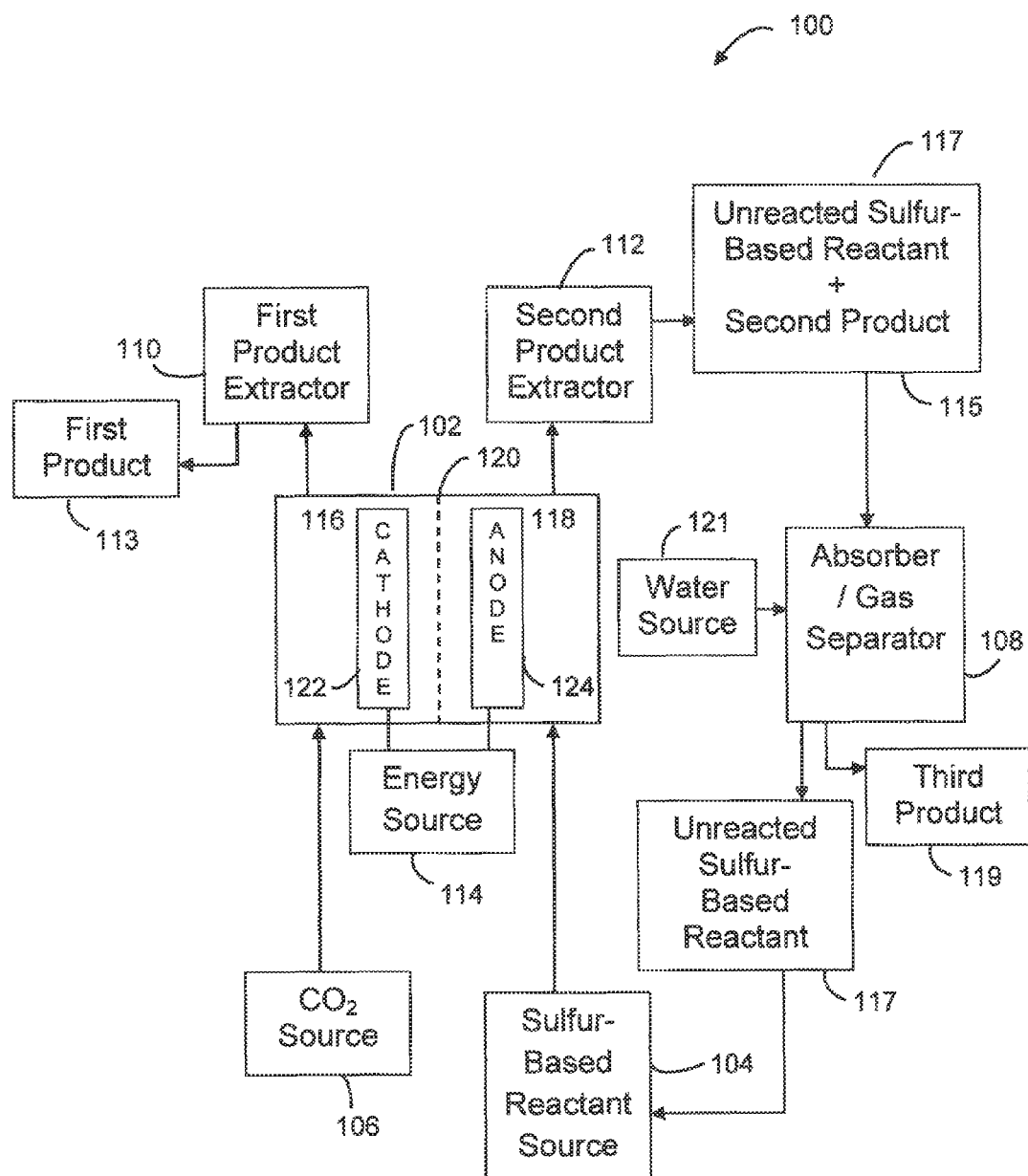


FIG. 1B

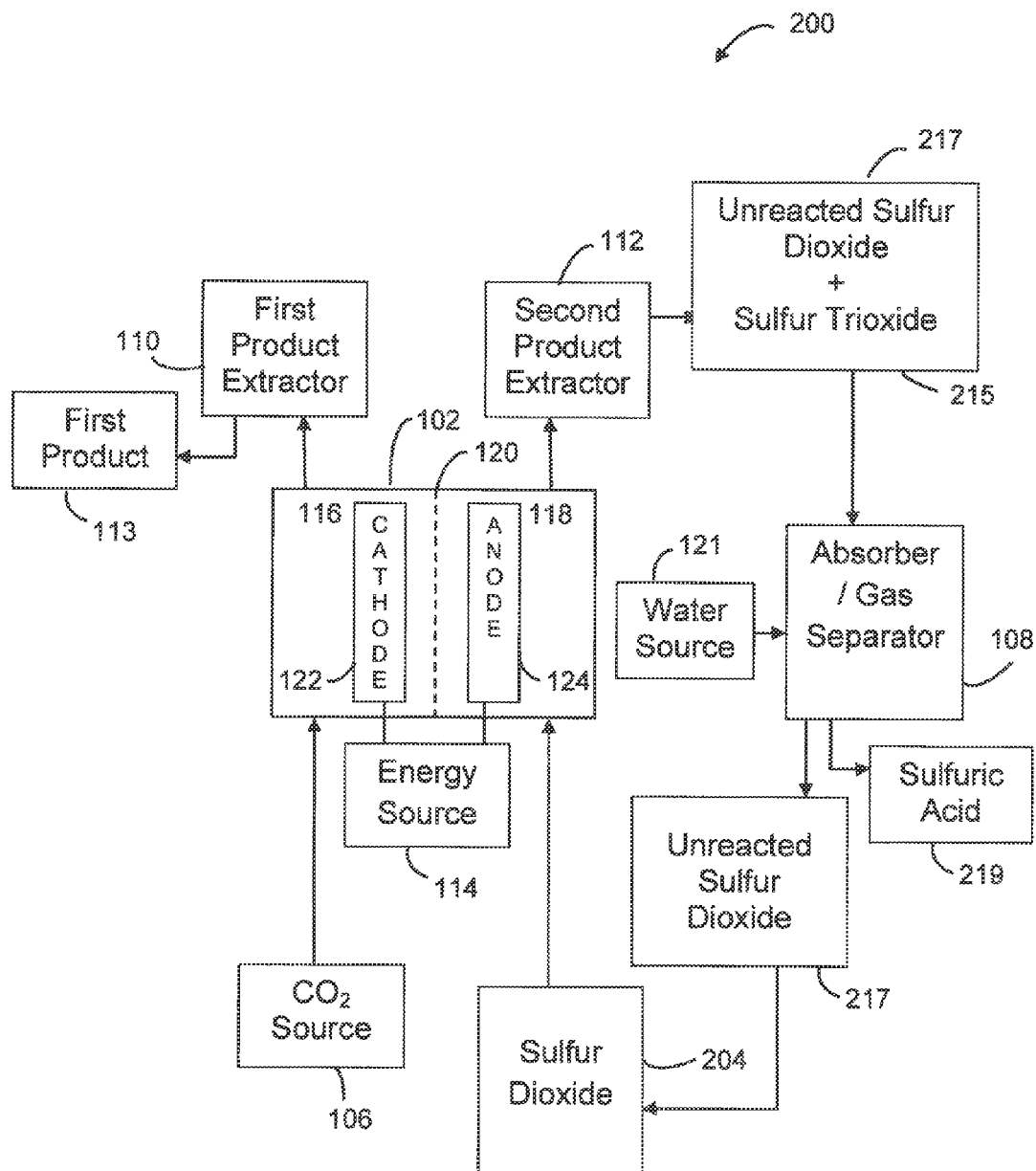


FIG. 2A

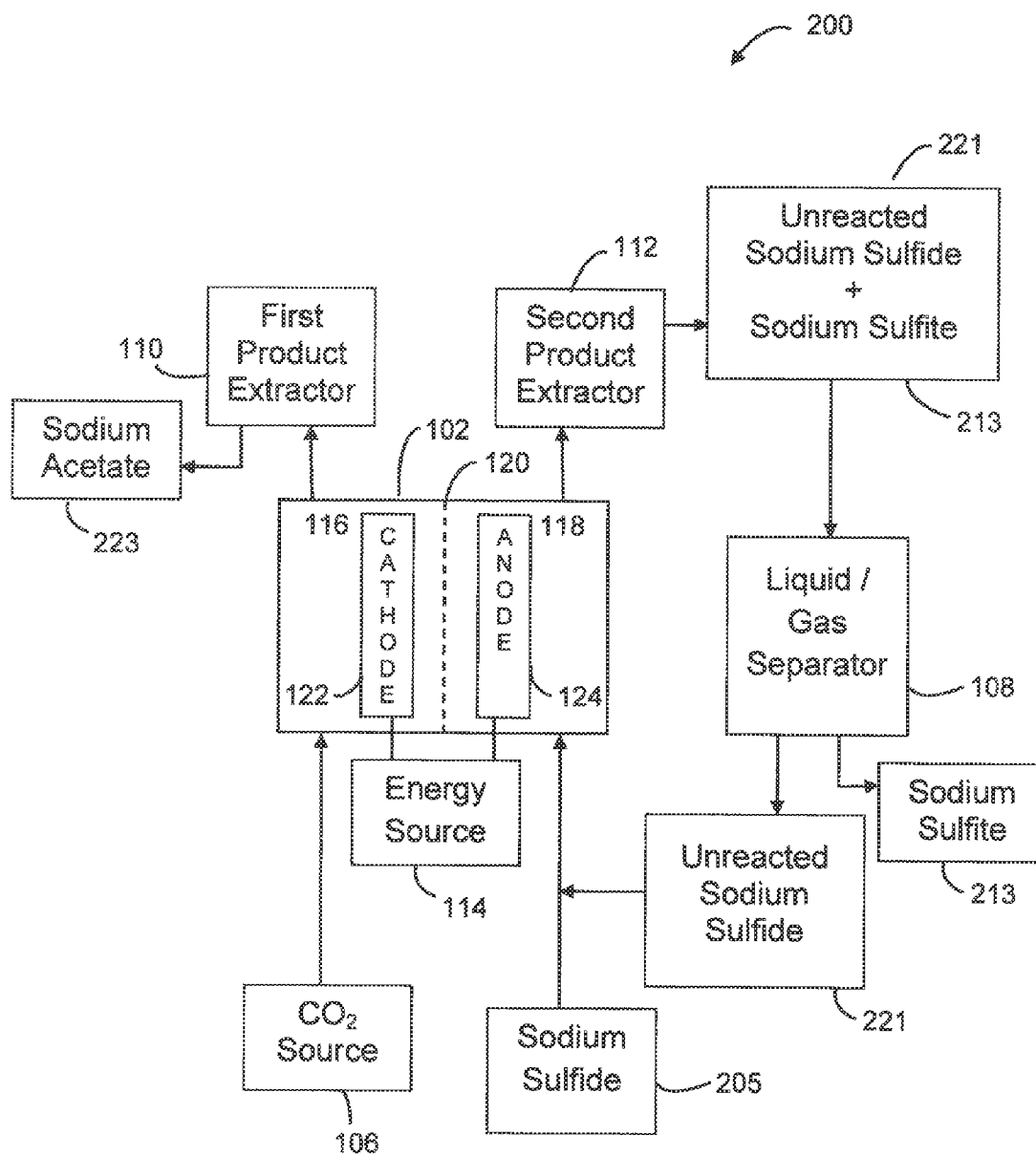


FIG. 2B

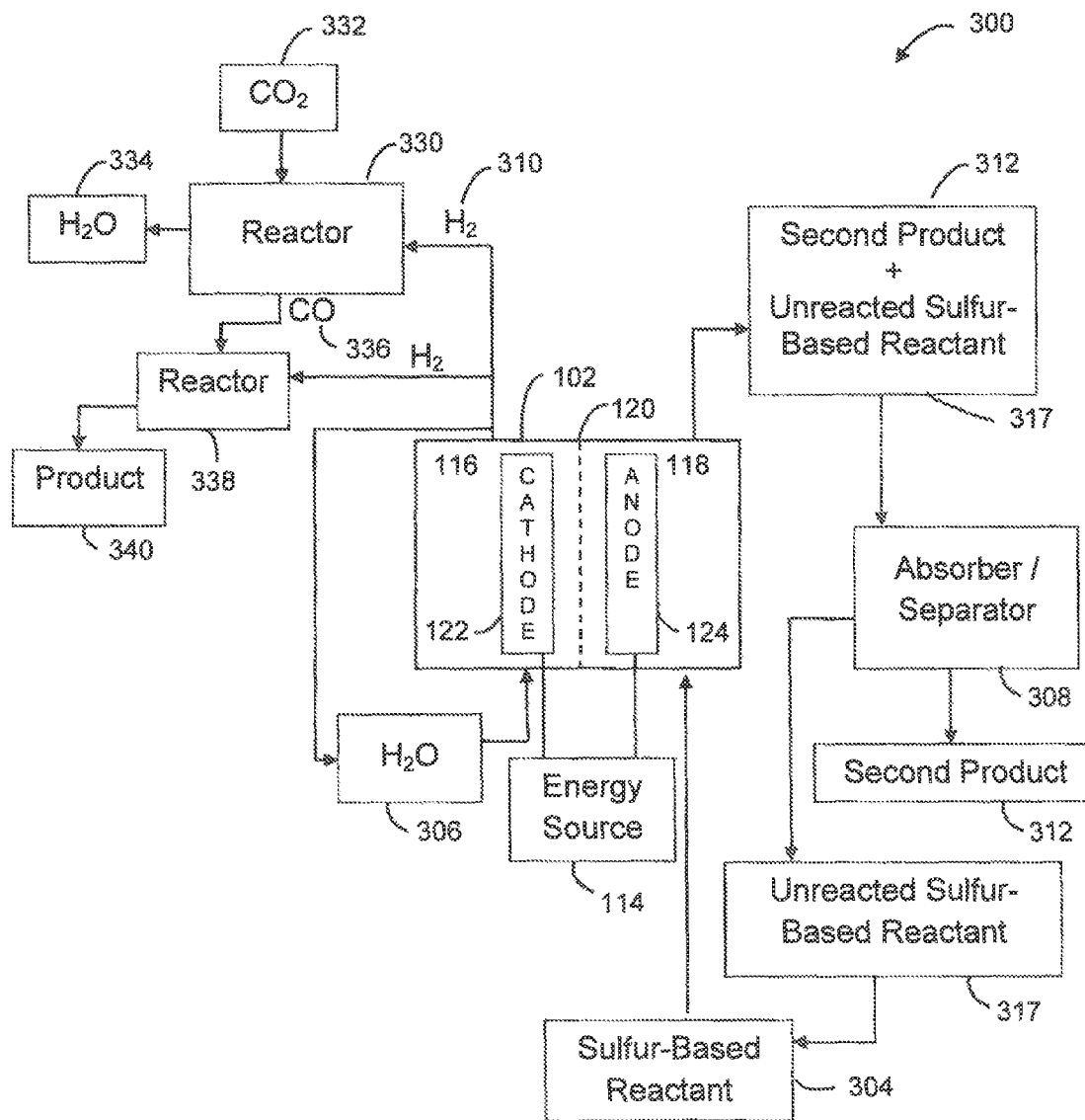


FIG. 3A

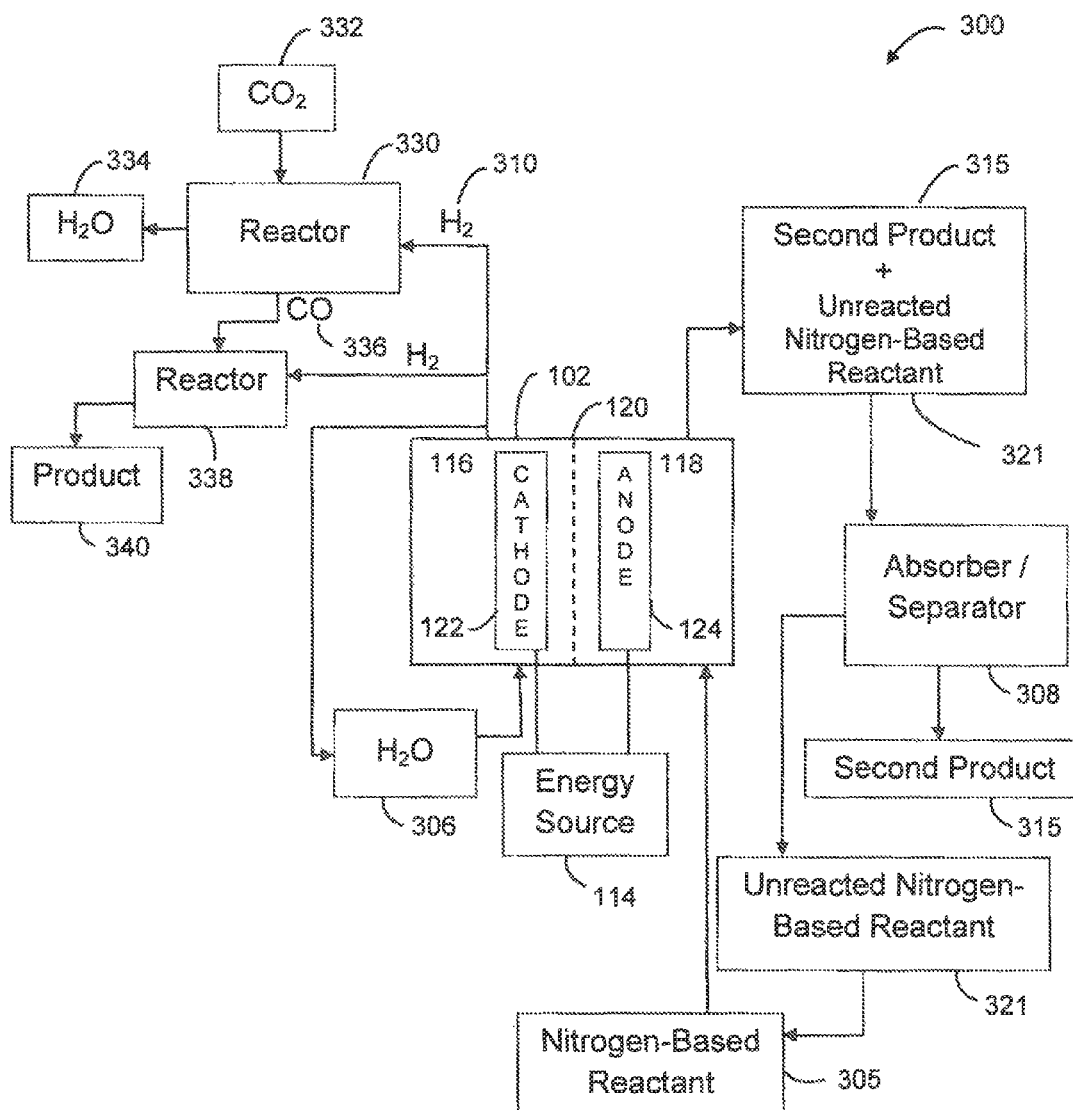


FIG. 3B

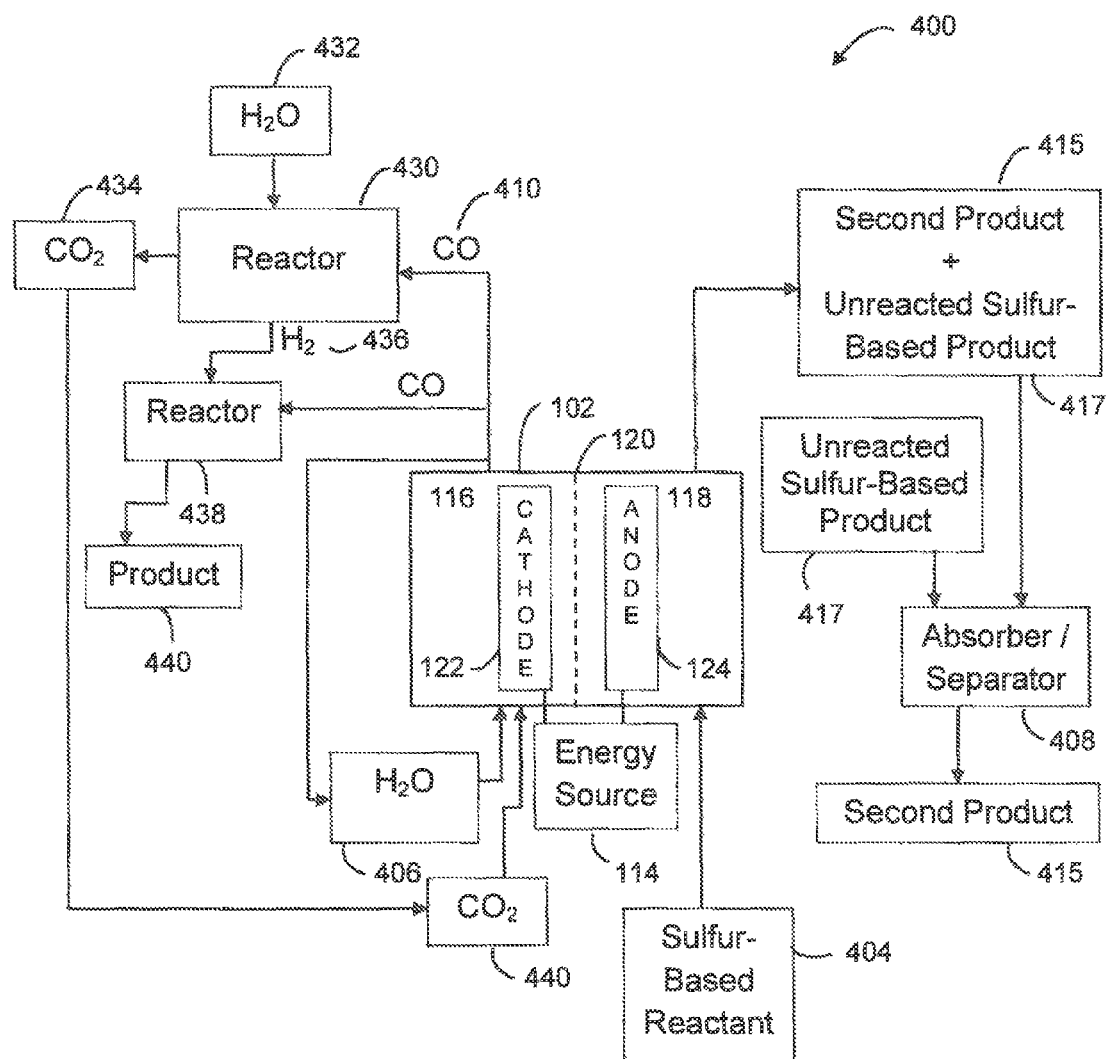


FIG. 4A

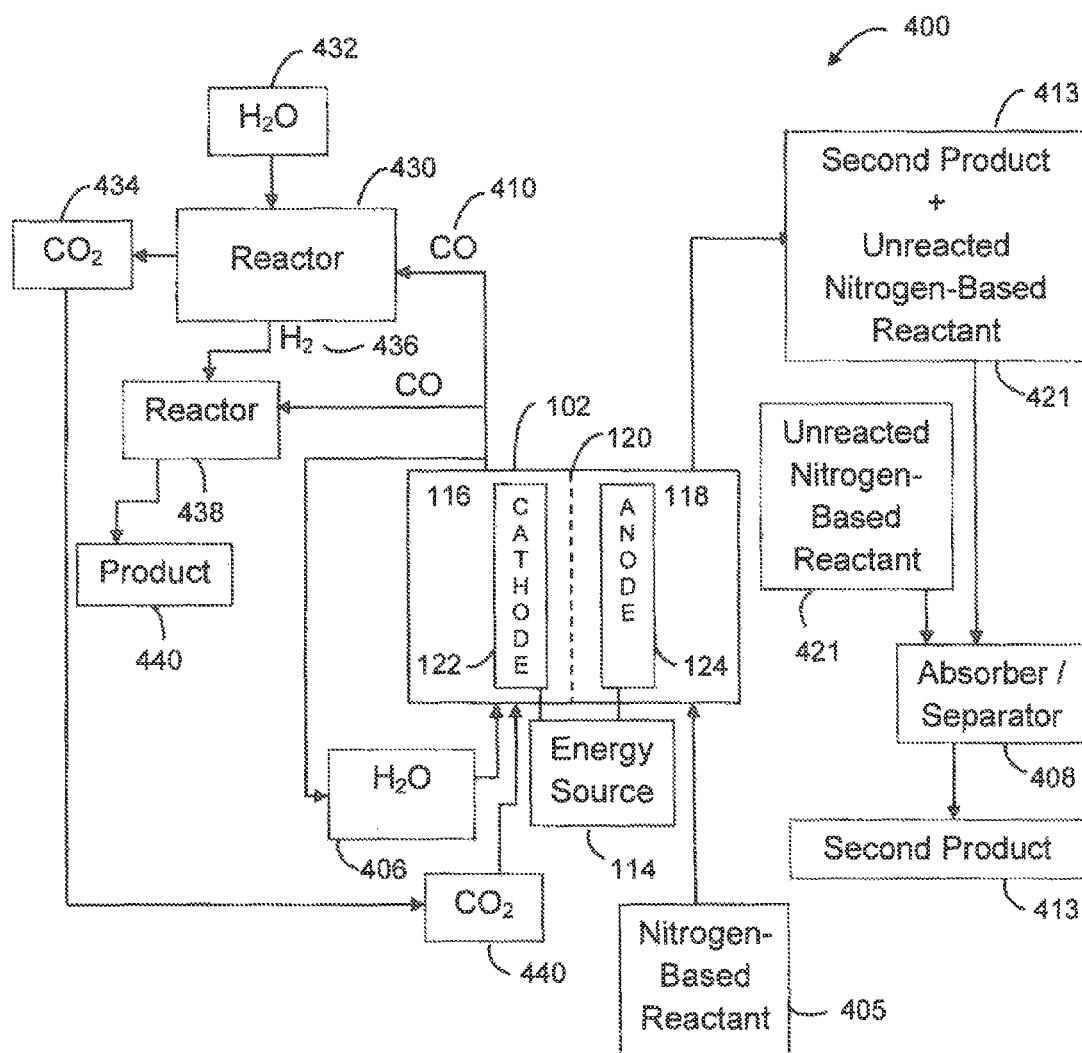


FIG. 4B

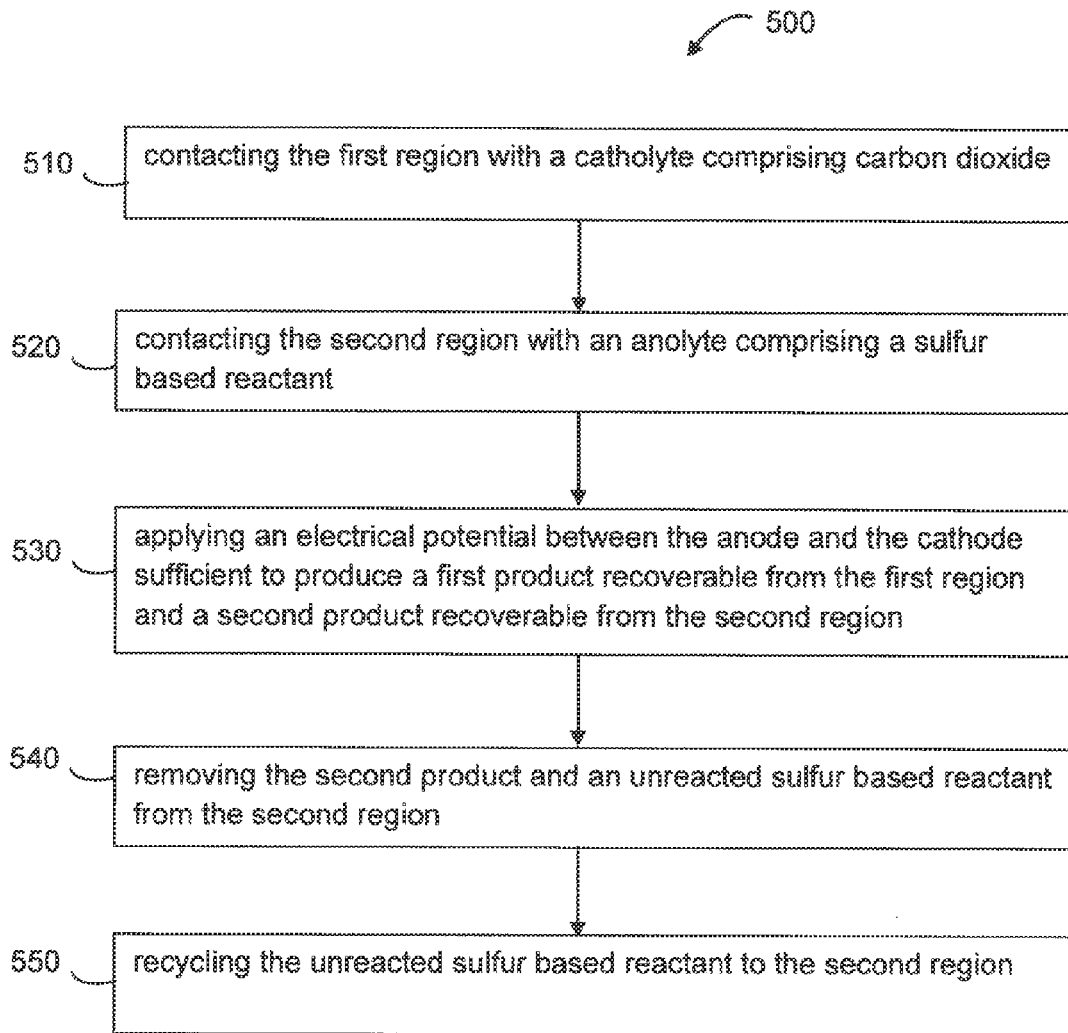


FIG. 5

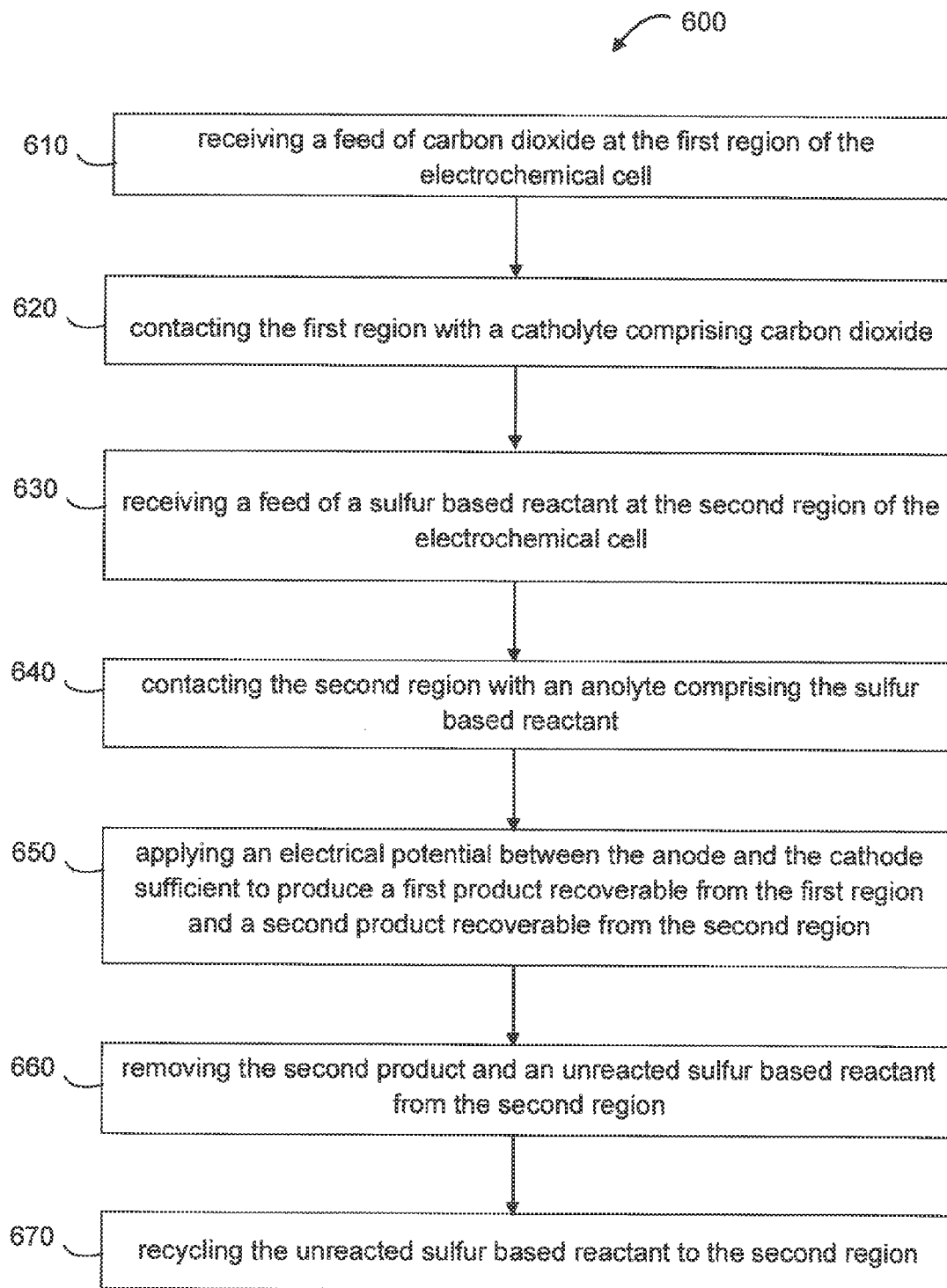


FIG. 6

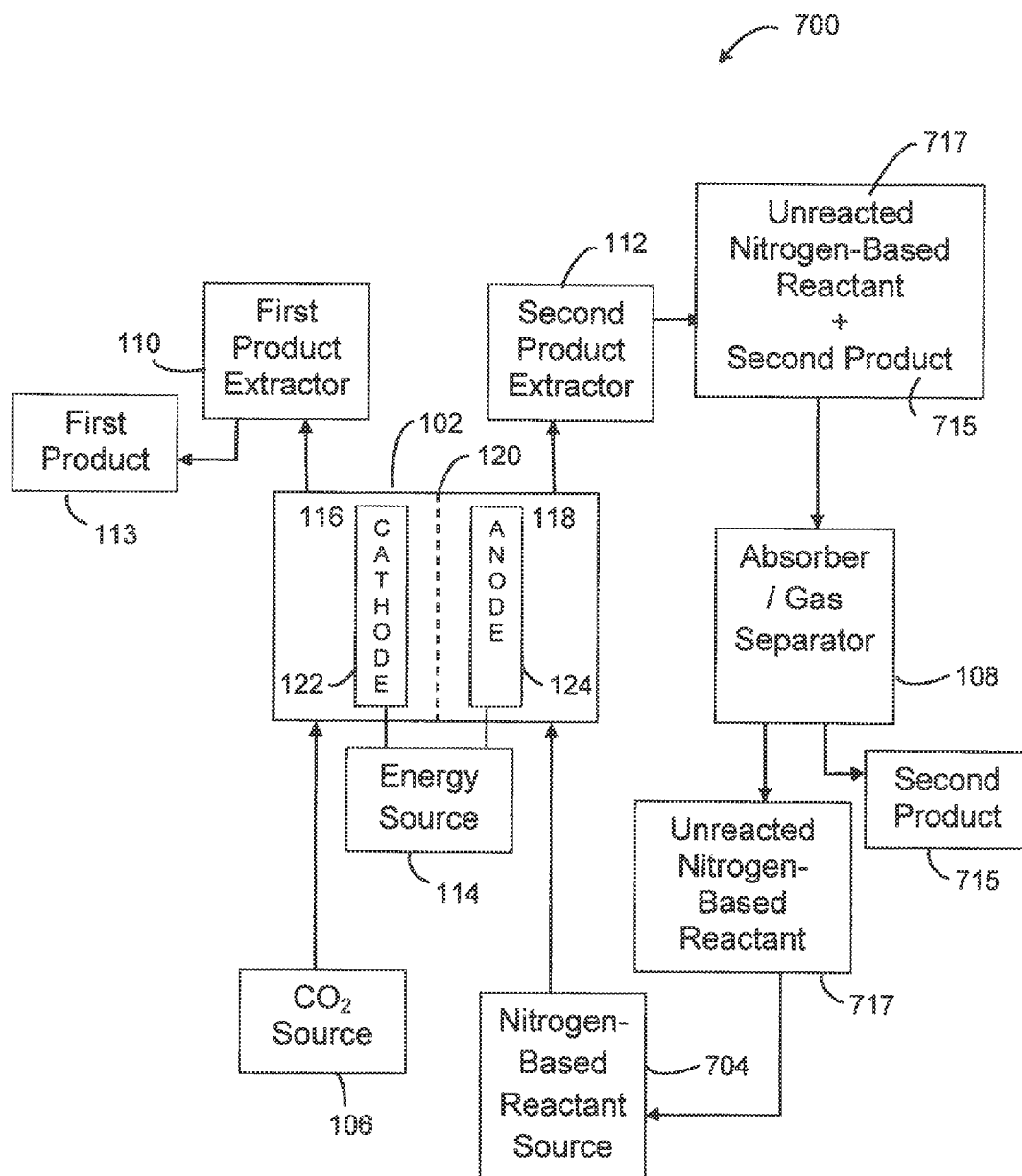


FIG. 7

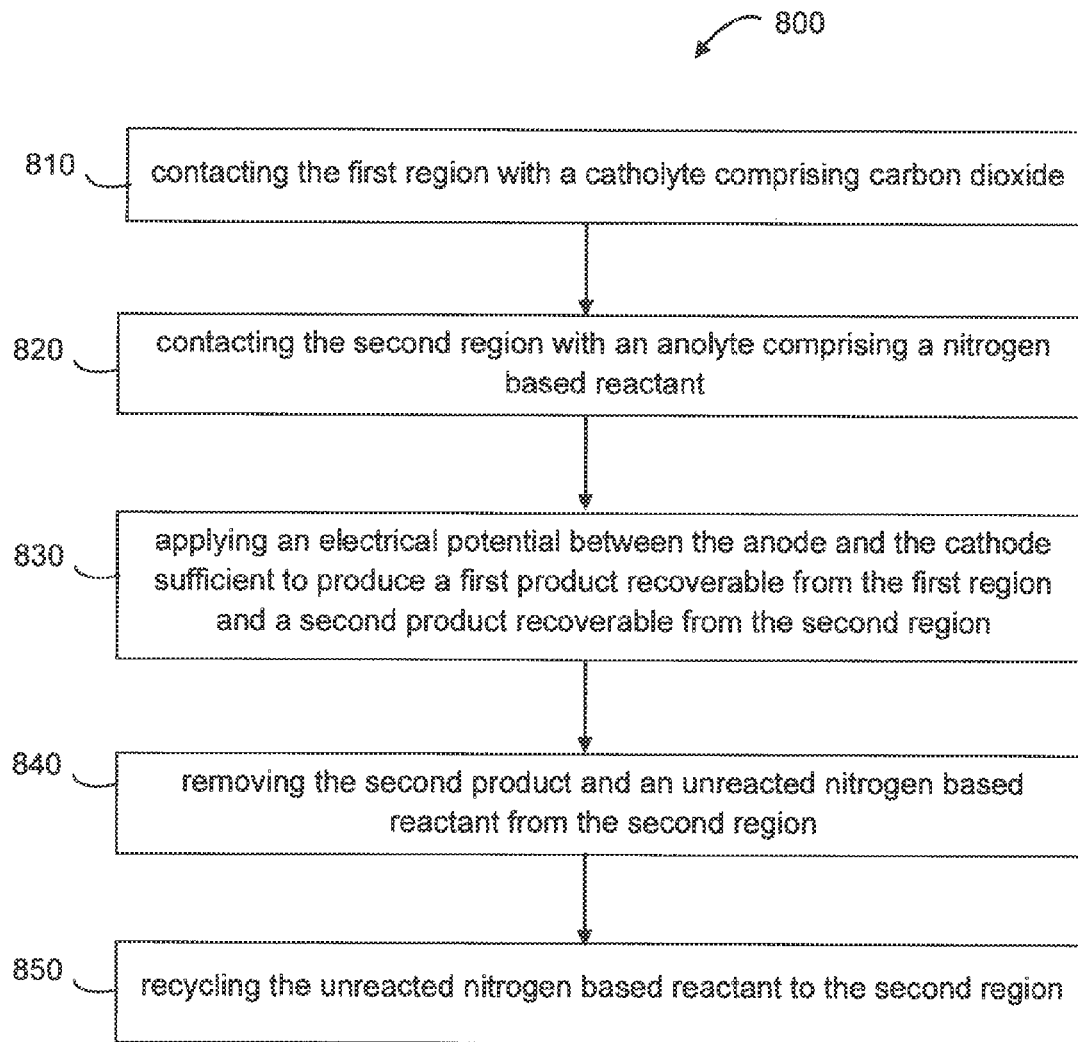


FIG. 8

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ELECTROCHEMICAL CO-PRODUCTION OF CHEMICALS WITH SULFUR-BASED REACTANT FEEDS TO ANODE

CROSS-REFERENCE TO RELATED APPLICATIONS

The present application claims the benefit under 35 U.S.C. §119(e) of U.S. Provisional Application Ser. No. 61/720,670 filed Oct. 31, 2012, U.S. Provisional Application Ser. No. 61/703,234 filed Sep. 19, 2012 and U.S. Provisional Application Ser. No. 61/675,938 filed Jul. 26, 2012. Said U.S. Provisional Application Ser. No. 61/720,670 filed Oct. 31, 2012, U.S. Provisional Application Ser. No. 61/703,234 filed Sep. 19, 2012 and U.S. Provisional Application Ser. No. 61/675,938 filed Jul. 26, 2012 are incorporated by reference in their entireties.

The present application also claims the benefit under 35 U.S.C. §119(e) of U.S. Provisional Application Ser. No. 61/703,229 filed Sep. 19, 2012, U.S. Provisional Application Ser. No. 61/703,158 filed Sep. 19, 2012, U.S. Provisional Application Ser. No. 61/703,175 filed Sep. 19, 2012, U.S. Provisional Application Ser. No. 61/703,231 filed Sep. 19, 2012, U.S. Provisional Application Ser. No. 61/703,232 filed Sep. 19, 2012, U.S. Provisional Application Ser. No. 61/703,238 filed Sep. 19, 2012, U.S. Provisional Application Ser. No. 61/703,187 filed Sep. 19, 2012. The U.S. Provisional Application Ser. No. 61/703,229 filed Sep. 19, 2012, U.S. Provisional Application Ser. No. 61/703,158 filed Sep. 19, 2012, U.S. Provisional Application Ser. No. 61/703,175 filed Sep. 19, 2012, U.S. Provisional Application Ser. No. 61/703,231 filed Sep. 19, 2012, U.S. Provisional Application Ser. No. 61/703,232 filed Sep. 19, 2012, U.S. Provisional Application Ser. No. 61/703,234 filed Sep. 19, 2012 and U.S. Provisional Application Ser. No. 61/703,187 filed Sep. 19, 2012 are hereby incorporated by reference in their entireties.

The present application incorporates by reference U.S. patent application Ser. No. 13/724,339 filed Dec. 21, 2012, now U.S. Pat. No. 9,175,407, U.S. patent application Ser. No. 13/724,878 filed Dec. 21, 2012, now U.S. Pat. No. 8,647,493, U.S. patent application Ser. No. 13/724,647 filed Dec. 21, 2012, now U.S. Pat. No. 8,845,876, U.S. patent application Ser. No. 13/724,231 filed Dec. 21, 2012, now U.S. Pat. No. 8,845,875, U.S. patent application Ser. No. 13/724,807, filed Dec. 21, 2012, now U.S. Pat. No. 8,692,019, U.S. patent application Ser. No. 13/724,996 filed Dec. 21, 2012, now U.S. Pat. No. 8,691,069, U.S. patent application Ser. No. 13/724,082 filed Dec. 21, 2012, now U.S. Pat. No. 8,821,709, and U.S. patent application Ser. No. 13/724,768 filed Dec. 21, 2012 now U.S. Pat. No. 8,444,844 in their entireties.

TECHNICAL FIELD

The present disclosure generally relates to the field of electrochemical reactions, and more particularly to methods and/or systems for electrochemical co-production of chemicals with a sulfur-based or a nitrogen-based reactant feed to the anode.

BACKGROUND

The combustion of fossil fuels in activities such as electricity generation, transportation, and manufacturing produces billions of tons of carbon dioxide annually. Research since the 1970s indicates increasing concentrations of carbon dioxide in the atmosphere may be responsible for altering the Earth's climate, changing the pH of the ocean and other

2

potentially damaging effects. Countries around the world, including the United States, are seeking ways to mitigate emissions of carbon dioxide.

A mechanism for mitigating emissions is to convert carbon dioxide into economically valuable materials such as fuels and industrial chemicals. If the carbon dioxide is converted using energy from renewable sources, both mitigation of carbon dioxide emissions and conversion of renewable energy into a chemical form that can be stored for later use will be possible.

SUMMARY

The present disclosure includes a system and method for producing a first product from a first region of an electrochemical cell having a cathode and a second product from a second region of the electrochemical cell having an anode. The method may include a step of contacting the first region with a catholyte comprising carbon dioxide. The method may include another step of contacting the second region with an anolyte comprising a sulfur-based reactant. Further, the method may include a step of applying an electrical potential between the anode and the cathode sufficient to produce a first product recoverable from the first region and a second product recoverable from the second region. An additional step of the method may include removing the second product and an unreacted sulfur-based reactant from the second region and recycling the unreacted sulfur-based reactant to the second region.

It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only and are not necessarily restrictive of the present disclosure. The accompanying drawings, which are incorporated in and constitute a part of the specification, illustrate subject matter of the disclosure. Together, the descriptions and the drawings serve to explain the principles of the disclosure.

BRIEF DESCRIPTION OF THE DRAWINGS

The numerous advantages of the disclosure may be better understood by those skilled in the art by reference to the accompanying figures in which:

FIG. 1A is a block diagram of a system in accordance with an embodiment of the present disclosure;

FIG. 1B is a block diagram of a system in accordance with an embodiment of the present disclosure;

FIG. 2A is a block diagram of a system in accordance with another embodiment of the present disclosure;

FIG. 2B is a block diagram of a system in accordance with an additional embodiment of the present disclosure;

FIG. 3A is a block diagram of a system in accordance with an additional embodiment of the present disclosure;

FIG. 3B is a block diagram of a system in accordance with an additional embodiment of the present disclosure;

FIG. 4A is a block diagram of a system in accordance with an additional embodiment of the present disclosure;

FIG. 4B is a block diagram of a system in accordance with an additional embodiment of the present disclosure;

FIG. 5 is a flow diagram of a method of electrochemical co-production of products in accordance with an embodiment of the present disclosure;

FIG. 6 is a flow diagram of a method of electrochemical co-production of products in accordance with another embodiment of the present disclosure;

FIG. 7 is a block diagram of a system in accordance with another embodiment of the present disclosure; and

FIG. 8 a flow diagram of a method of electrochemical co-production of products in accordance with another embodiment of the present disclosure.

DETAILED DESCRIPTION

Reference will now be made in detail to the subject matter disclosed, which is illustrated in the accompanying drawings.

Referring generally to FIGS. 1-8, systems and methods of electrochemical co-production of products with either a sulfur-based reactant feed or a nitrogen-based reactant feed to an anode are disclosed. It is contemplated that the electrochemical co-production of products may include a production of a first product, such as reduction of carbon dioxide to sulfur-based products to include one, two, three, and four carbon chemicals, at a cathode side of an electrochemical cell with co-production of a second product, such as an oxidized sulfur-based product, at the anode of the electrochemical cell where the anolyte comprises a sulfur-based reactant. Some of the sulfur-based reactant may remain unreacted at the anode side of the electrochemical cell and this unreacted sulfur-based reactant may be recycled back to the anolyte.

A sulfur-based reactant may include an oxidizable sulfur compound. Sulfur-based reactants may include, for example, sulfur dioxide, sodium sulfide, potassium sulfide, and hydrogen sulfide. The sulfur-based reactant may comprise a waste gas from other chemical process or, for example, a coal burning power plant. One example may include hydrogen sulfide, which can come from natural gas processing and oil refinery processes.

Before any embodiments of the disclosure are explained in detail, it is to be understood that the embodiments may not be limited in application per the details of the structure or the function as set forth in the following descriptions or illustrated in the figures. Different embodiments may be capable of being practiced or carried out in various ways. Also, it is to be understood that the phraseology and terminology used herein is for the purpose of description and should not be regarded as limiting. The use of terms such as "including," "comprising," or "having" and variations thereof herein are generally meant to encompass the item listed thereafter and equivalents thereof as well as additional items. Further, unless otherwise noted, technical terms may be used according to conventional usage. It is further contemplated that like reference numbers may describe similar components and the equivalents thereof.

Referring to FIG. 1, a block diagram of a system 100 in accordance with an embodiment of the present disclosure is shown. System (or apparatus) 100 generally includes an electrochemical cell (also referred as a container, electrolyzer, or cell) 102, a sulfur-based reactant source 104, a carbon dioxide source 106, an absorber/gas separator 108, a first product extractor 110, a first product 113, a second product extractor 112, second product 115, and an energy source 114.

Electrochemical cell 102 may be implemented as a divided cell. The divided cell may be a divided electrochemical cell and/or a divided photoelectrochemical cell. Electrochemical cell 102 may include a first region 116 and a second region 118. First region 116 and second region 118 may refer to a compartment, section, or generally enclosed space, and the like without departing from the scope and intent of the present disclosure. First region 116 may include a cathode 122. Second region 118 may include an anode 124. First region 116 may include a catholyte whereby carbon dioxide is dissolved in the catholyte. Second region 118 may include an anolyte which may include a sulfur-based reactant, as well as unreacted sulfur-based reactant that is recycled into the anolyte after going through the second product extractor 112 and the absorber/gas separator 108. Energy source 114 may generate

an electrical potential between the anode 124 and the cathode 122. The electrical potential may be a DC voltage. Energy source 114 may be configured to supply a variable voltage or constant current to electrochemical cell 102. Separator 120 may selectively control a flow of ions between the first region 116 and the second region 118. Separator 120 may include an ion conducting membrane or diaphragm material.

Electrochemical cell 102 is generally operational to reduce carbon dioxide in the first region 116 to a first product 113 recoverable from the first region 116 while producing a second product 115 recoverable from the second region 118. Cathode 122 may reduce the carbon dioxide into a first product 113 that may include one or more compounds. Examples of the first product 113 recoverable from the first region by first product extractor 110 may include CO, formic acid, formaldehyde, methanol, oxalate, oxalic acid, glyoxylic acid, glycolic acid, glyoxal, glycolaldehyde, ethylene glycol, acetic acid, acetaldehyde, ethanol, ethylene, ethane, lactic acid, propanoic acid, acetone, isopropanol, 1-propanol, 1,2-propylene glycol, propylene, propane, 1-butanol, 2-butanol, butane, butene, butadiene, a carboxylic acid, a carboxylate, a ketone, an aldehyde, and an alcohol.

Carbon dioxide source 106 may provide carbon dioxide to the first region 116 of electrochemical cell 102. In some embodiments, the carbon dioxide is introduced directly into the region 116 containing the cathode 122. It is contemplated that carbon dioxide source may include a source of a mixture of gases in which carbon dioxide has been filtered from the gas mixture.

First product extractor 110 may implement an organic product and/or inorganic product extractor. First product extractor 110 is generally operational to extract (separate) the first product 113 from the first region 116. The extracted first product 113 may be presented through a port of the system 100 for subsequent storage and/or consumption by other devices and/or processes.

The anode side of the reaction occurring in the second region 118 may include a sulfur-based reactant, which may be a gas phase, liquid phase, or solution phase reactant. In addition, the sulfur-based reactant may also include a nitrogen based reactant. A sulfur-based reactant and a nitrogen-based reactant may both be fed to the anolyte, or only a sulfur-based or only a nitrogen-based reactant may be fed to the anolyte. The second product 115 recoverable from the second region 118 may be derived from a variety of oxidations such as the oxidation of inorganic sulfur-based compounds as well as organic sulfur compounds. Oxidations may be direct, such as the gas phase conversion of sulfur dioxide to sulfur trioxide at the anode. The oxidations also may be solution phase, such as the oxidation of sodium sulfide to sodium sulfite or sodium thiosulfate. In addition, the second product 115 recoverable from the second region 118 may be derived from a variety of oxidations such as the oxidation of inorganic nitrogen-based compounds as well as organic nitrogen compounds. Examples are in the table below.

TABLE 1

Chemical Feed to Anode	Oxidation Product(s)
Sulfur dioxide (gas phase)	Sulfur trioxide, sulfuric acid
Sulfur dioxide (aqueous solution)	Hydrogen sulfite, sulfuric acid, Alkali metal sulfites, thiosulfates, polysulfides, sulfates
Alkali Metal Sulfides	Alkali metal sulfates, thiosulfates, polysulfides
Alkali Metal Sulfites	Alkali metal sulfite, thiosulfates, polysulfides, sulfates

TABLE 1-continued

Chemical Feed to Anode	Oxidation Product(s)
Alkali Metal Thiosulfates	Alkali metal polysulfides, sulfates
Hydrogen Sulfide	Sulfur, thiosulfate, sulfite, sulfate, sulfuric acid
Nitric Oxide (Nitrogen monoxide)	Nitrite, nitrate, nitric acid
Nitrous Oxide	Nitrite, nitrate, nitric acid
Nitrogen Dioxide	Nitric acid
Ammonia	N ₂ , nitrite, nitrate, nitric acid

Second product extractor **112** may extract the second product **115** from the second region **118**. The extracted second product **115** may be presented through a port of the system **100** for subsequent storage and/or consumption by other devices and/or processes. The second product extractor **112** may also extract unreacted sulfur-based reactant **117** from the second region **118**, which may be recycled back to the anolyte. It is contemplated that first product extractor **110** and/or second product extractor **112** may be implemented with electrochemical cell **102**, or may be remotely located from the electrochemical cell **102**. Additionally, it is contemplated that first product extractor **110** and/or second product extractor **112** may be implemented in a variety of mechanisms and to provide desired separation methods, such as fractional distillation, without departing from the scope and intent of the present disclosure.

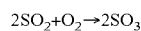
Furthermore, the second product **115** as well as unreacted sulfur-based reactant **117** may be extracted from the second region **118** and presented to absorber/gas separator **108**. The absorber/gas separator may separate the second product **115** from the unreacted sulfur-based reactant **117**, as shown in FIG. 1A.

The absorber/gas separator **108** may also absorb the second product **115** in water provided by water source **121**, which may form a third product **119** as shown in FIG. 1B. For example, the sulfur-based reactant source **104** may be sulfur dioxide in one embodiment, which results in the formation of sulfur trioxide as the second product **115**. The second product extractor **112** may extract the second product **115** and the unreacted sulfur-based reactant **117**, which is provided to absorber/gas separator **108**. Water is provided to the absorber/gas separator **108** via water source **121** which may cause the second product **115** to form a third product **119**. In the example, sulfur trioxide may be absorbed with the water to form sulfuric acid (third product **119**). The absorber/gas separator **108** also separates the third product **119** and unreacted sulfur-based reactant **117**. Unreacted sulfur-based reactant **117** may be recycled back to the second region **118** as an input feed to the second region **118** of electrochemical cell **102**. It is contemplated that unreacted sulfur-based reactant **117** may be supplied as a sole or as an additional input feed to the second region **118** of the electrochemical cell **102** without departing from the scope and intent of the present disclosure.

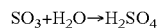
The absorber/gas separator **108** may include an apparatus that absorbs a in input in water or another substance. The absorber/gas separator **108** may include a mechanism for separating one gas from another gas, or a gas from a liquid such as packed bed gas stripping/adsorption column or distillation column.

Through the co-production of a first product **113** and a second product **115**, the overall energy requirement for making each of the first product **113** and second product **115** may be reduced by 50% or more. In addition, electrochemical cell **102** may be capable of simultaneously producing two or more products with high selectivity.

A preferred embodiment of the present disclosure may include production of organic chemicals, such as carbon dioxide reduction products, at the cathode while simultaneously using a sulfur-based reactant feed to the anode for use in the oxidation of sulfur-based products. Referring to FIG. 2A, system **200** for co-production of a first product **113** and sulfuric acid **219** is shown. In the system **200**, sulfur dioxide **204** is supplied to the second region **118** where it is oxidized to produce sulfur trioxide **115**. The oxidation of sulfur dioxide **204** to produce sulfur trioxide **115** is as follows:

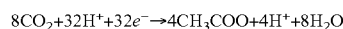


The oxidation of the sulfur dioxide **204** in the presence of some water may produce protons that are utilized to reduce carbon dioxide at the cathode. Both the sulfur trioxide **215** and the unreacted sulfur-based reactant **117** may be fed into an absorber/gas separator **108**. The sulfur trioxide **215** may be absorbed in water provided by water source **121** to produce sulfuric acid **219**, according to the following reaction:



Any unreacted sulfur dioxide **217** may be recycled back to the second region **118**. The unreacted sulfur dioxide **217** may be recycled back to the second region either as a pure anhydrous gas or in a liquid phase. The gas phase may be generally preferred in order to minimize energy requirements.

The cathode reaction may include the production of a first product **113**, such as a carbon dioxide reduction product. In the example shown in FIG. 2A, the first product **113** may include acetic acid, although it is contemplated that other products may be produced at first region **116** without departing from the scope of the current disclosure. If the first product **113** is acetic acid, the cathode reaction is the formation of acetate or acetic acid as follows:



Referring to FIG. 2B, a block diagram of a system **200** in accordance with an additional embodiment of the present disclosure is provided. Similar to the embodiment shown in FIG. 2A, FIG. 2B is a block diagram of a system in accordance with an additional embodiment of the present disclosure wherein a sulfur-based reactant source may be oxidized at the anode to produce inorganic alkali metal sulfur compounds and a corresponding alkali metal hydroxide at the cathode. For example, system **200** may include a sodium sulfide source **205**, which may be in liquid phase such as in an aqueous solution. The sodium sulfide **205** is fed to the second region **118** where it is oxidized to produce sodium sulfite **213**. The sodium sulfite **213** and any unreacted sodium sulfide **221** may be extracted from the second region **118** and separated by liquid/gas separator **108** which may also be an evaporator/crystallizer to separate the sodium sulfide from the sulfite using the water solubility differences of the two compounds in an aqueous solution. The unreacted sodium sulfide **221** may be recycled back to the second region **118**. The carbon dioxide reduction product may be sodium acetate **223** when the reactant is sodium sulfide **205**. Other reactants will yield different products. For example, for other alkali sulfide and inorganics, the product may be the corresponding alkali metal organic carbon compound salts.

The reaction shown in FIG. 2B may occur under alkaline conditions, and the reduction reaction in the first region **116** may utilize sodium cations produced in the oxidation reaction in order to produce the first product.

In the example shown in FIG. 2B where the sodium sulfide **205** may be fed into the anolyte in a solution, the sodium sulfide anolyte concentration may be in the range of 2 wt % to

about 40 wt %, more preferably in the range of 5 wt % to 35 wt %, and more preferably in the 10 wt % to 30 wt % range.

The example shown in FIG. 2B may also be used to produce sodium thiosulfate at the anode when sodium sulfide **205** is the sulfur-based reactant source. Similarly, other alkali metal sulfides may be used instead of sodium sulfide. For example, potassium sulfide may serve as the sulfur-based reactant source at the anode in order to produce potassium sulfite, potassium thiosulfate, potassium polysulfides, and potassium sulfates. The final oxidation product(s) from the oxidation of the sulfide may depend on a number of factors including the operating pH of the anolyte, the selected anode electrocatalyst as well as the incorporation of any catalysts in the second region space, and the extent of oxidation of the reactant which may depend on the rate of flow of the reactant through the anolyte. The reaction may occur under alkaline conditions, and the reduction reaction in the first region **116** may utilize potassium cations produced in the oxidation reaction in order to produce the corresponding alkali metal carbon product, such as potassium acetate.

It is contemplated that reactions occurring at the first region **116** may occur in a catholyte which may include water, sodium bicarbonate or potassium bicarbonate, or other catholytes. The reactions occurring at the second region **118** may be in a gas phase, for instance in the case of gas phase reactant **118** such as sulfur dioxide. The reaction at the second region **118** may also occur in liquid phase, such as the case of an alkali metal sulfide in solution.

Referring to FIGS. 3A, 3B, 4A and 4B, block diagrams of systems **300**, **400** in accordance with additional embodiments of the present disclosure are shown. Systems **300**, **400** provide additional embodiments to systems **100**, **200** of FIGS. 1A and B and 2A and B to co-produce a first product and second product.

Referring specifically to FIG. 3A, first region **116** of electrochemical cell **102** may produce a first product of H₂ **310** which is combined with carbon dioxide **332** in a reactor **330** which may perform a reverse water gas shift reaction. This reverse water gas shift reaction performed by reactor **330** may produce water **334** and carbon monoxide **336**. Carbon monoxide **336** along with H₂ **310** may be combined at reactor **338**. Reactor **338** may cause a reaction by utilizing H₂ **310** from the first region **116** of the electrochemical cell **102**, such as a Fischer-Tropsch-type reaction, to reduce carbon monoxide to a product **340**. Product **340** may include methane, methanol, hydrocarbons, glycols, olefins. Water **306** may be an additional product produced by the first region **116** and may be recycled as an input feed to the first region **116**. Reactor **338** may also include transition metals such as iron, cobalt, and ruthenium as well as transition metal oxides as catalysts that are deposited on inorganic support structures that may promote the reaction of CO with hydrogen at lower temperatures and pressures.

Second region **118** may co-produce a second product **312**, such as sulfuric acid, from a sulfur-based reactant **304**, such as sulfur dioxide. Unreacted sulfur-based reactant **317** may be separated from the second product **312** and recycled back as an input feed to the second region **118**. It is contemplated that sulfur-based reactant **304** may include a range of sulfur-based reactants, including alkali metal sulfides, alkali metal sulfites, alkali metal bisulfites, alkali metal thiosulfates, and hydrogen sulfide while second product **312** may also refer to any type of sulfur compound that may be the oxidation product from the sulfur-based reactant, including sulfur trioxide, sulfuric acid, alkali metal sulfites, alkali metal thiosulfates as well as alkali metal polysulfides without departing from the scope or intent of the present disclosure.

Referring to FIG. 3B, it is contemplated that second region **118** may co-produce a second product **315**, from a nitrogen-based reactant **305**, such as nitrogen dioxide or nitric oxide to produce second product **315**. Second product **315** may include nitric acid, nitrogen gas, or another product. Unreacted nitrogen-based reactant **321** may be separated from the second product **315** and recycled back as an input feed to the second region **118**.

Referring to FIG. 4A, first region **116** of electrochemical cell **102** may produce a first product of carbon monoxide **410** which is combined with water **432** in a reactor **430** which may perform a water gas shift reaction. This water gas shift reaction performed by reactor **430** may produce carbon dioxide **434** and H₂ **436**. Carbon monoxide **410** and H₂ **436** may be combined at reactor **438**. Reactor **438** may cause a reaction, such as a Fischer-Tropsch-type reaction, to reduce carbon monoxide to a product **440**. Product **440** may include methane, methanol, hydrocarbons, glycols, olefins by utilizing H₂ **436** from the water gas shift reaction. Carbon dioxide **434** may be a byproduct of water gas shift reaction of reactor **430** and may be recycled as an input feed to the first region **116**. Water **406** may be an additional product produced by the first region **116** and may be recycled as another input feed to the first region **116**. Reactor **438** may also include transition metals such as iron and copper as well as transition metal oxides as catalysts, deposited on inorganic support structures that may promote the reaction of CO with hydrogen at lower temperatures and pressures.

Second region **118** of electrochemical cell **102** may co-produce a second product **415**, such as sulfuric acid, from a sulfur-based reactant **404**, such as sulfur dioxide. Unreacted sulfur-based reactant **417** may be separated from the second product **415** and recycled back as an input feed to the second region **118**. It is contemplated that sulfur-based reactant **404** may include a range of sulfur-based reactants, including alkali metal sulfides, alkali metal sulfites, alkali metal bisulfites, alkali metal thiosulfates, and hydrogen sulfide while second product **415** may also refer to any type of sulfur compound that may be oxidized from the sulfur-based reactant **404**, including sulfur trioxide, sulfuric acid, alkali metal sulfites and thiosulfates as well as alkali metal polysulfides without departing from the scope or intent of the present disclosure.

Referring to FIG. 4B, it is contemplated that second region **118** may co-produce a second product **413**, from a nitrogen-based reactant **405**, such as nitrogen dioxide or nitric oxide to produce second product **413**. Unreacted nitrogen-based reactant **421** may be separated from the second product **413** and recycled back as an input feed to the second region **118**.

Referring to FIG. 5 a flow diagram of a method **500** of electrochemical co-production of products in accordance with an embodiment of the present disclosure is shown. It is contemplated that method **500** may be performed by systems **100** and system **200** as shown in FIGS. 1A-B and 2A-B. Method **500** may include producing a first product from a first region of an electrochemical cell having a cathode and a second product from a second region of the electrochemical cell having an anode.

Method **500** of electrochemical co-production of products may include a step of contacting the first region with a catholyte comprising carbon dioxide **510**. A further step of method **500** may include contacting the second region with an anolyte comprising a sulfur-based reactant **520**. The method **500** also includes the step of applying an electrical potential between the anode and the cathode sufficient to produce a first product recoverable from the first region and a second product recoverable from the second region **530**. The method **500**

also includes the step of removing the second product and an unreacted sulfur-based reactant from the second region **540** and recycling the unreacted sulfur-based reactant to the second region **550**. Advantageously, a first product produced at the first region may be recoverable from the first region and a second product produced at the second region may be recoverable from the second region.

Referring to FIG. 6, a flow diagram of a method **600** of electrochemical co-production of products in accordance with another embodiment of the present disclosure is shown. It is contemplated that method **600** may be performed by system **100** and system **200** as shown in FIGS. 1A-B and 2A-B. Method **600** may include steps for producing a first product from a first region of an electrochemical cell having a cathode and a second product from a second region of the electrochemical cell having an anode.

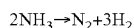
Method **600** may include a step of receiving a feed of carbon dioxide at the first region of the electrochemical cell **610** and contacting the first region with a catholyte comprising carbon dioxide **620**. Method **600** also includes the step of receiving a feed of a sulfur-based reactant at the second region of the electrochemical cell **630** and contacting the second region with an anolyte comprising the sulfur-based reactant **640**. A further step of the method is to apply an electrical potential between the anode and the cathode sufficient to produce a first product recoverable from the first region and a second product recoverable from the second region **650**. The method **600** also includes the step of removing the second product and an unreacted sulfur-based reactant from the second region **660**. The method **600** also includes the step of recycling the unreacted sulfur-based reactant to the second region **670**.

It is contemplated that a receiving feed may include various mechanisms for receiving a supply of a product, whether in a continuous, near continuous or batch portions.

In an additional embodiment of the present disclosure, nitrogen compounds can also be oxidized at the anode as shown in FIG. 7. System **700** depicted in FIG. 7 includes nitrogen-based reactant source **704** which is provided to the second region **118**. Nitrogen-based reactant source **704** may include nitric oxide, nitrous oxide, or ammonia, as well as other nitrogen compounds. For example, the nitrogen-based reactant source may be in aqueous solution and could include an alkali metal nitrite, nitrates and their mixtures.

Nitrogen-based reactant source **704** is reacted at the anode to produce second product **715**. Second product **715** may include nitrogen gas or nitric acid. Unreacted nitrogen-based reactant **717** may be separated from the second product **715** using the absorber/gas separator **108** and recycled back to the second region **118**.

In one example, the nitrogen-based reactant source **704** is ammonia, which is oxidized to produce second product **715** of nitrogen as well as hydrogen. This formation of hydrogen can be useful for processes requiring hydrogen while not producing any co-current carbon dioxide. The reaction is:



Referring to FIG. 8 a flow diagram of a method **800** of electrochemical co-production of products in accordance with an embodiment of the present disclosure is shown. It is contemplated that method **800** may be performed by system **700** as shown in FIG. 7. Method **800** may include producing a first product from a first region of an electrochemical cell having a cathode and a second product from a second region of the electrochemical cell having an anode.

Method **800** of electrochemical co-production of products may include a step of contacting the first region with a

catholyte comprising carbon dioxide **810**. A further step of method **800** may include contacting the second region with an anolyte comprising a nitrogen-based reactant **820**. The method **800** also includes the step of applying an electrical potential between the anode and the cathode sufficient to produce a first product recoverable from the first region and a second product recoverable from the second region **830**. The method **800** also includes the step of removing the second product and an unreacted nitrogen-based reactant from the second region **840** and recycling the unreacted nitrogen-based reactant to the second region **850**.

It is contemplated that the structure and operation of the electrochemical cell **102** may be adjusted to provide desired results. For example, the electrochemical cell **102** may operate at higher pressures, such as pressure above atmospheric pressure which may increase current efficiency and allow operation of the electrochemical cell at higher current densities.

Additionally, the cathode **122** and anode **124** may include a high surface area electrode structure with a void volume which may range from 30% to 98%. The electrode void volume percentage may refer to the percentage of empty space that the electrode is not occupying in the total volume space of the electrode. The advantage in using a high void volume electrode is that the structure has a lower pressure drop for liquid flow through the structure. The specific surface area of the electrode base structure may be from $2 \text{ cm}^2/\text{cm}^3$ to $500 \text{ cm}^2/\text{cm}^3$ or higher. The electrode specific surface area is a ratio of the base electrode structure surface area divided by the total physical volume of the entire electrode. It is contemplated that surface areas also may be defined as a total area of the electrode base substrate in comparison to the projected geometric area of the current distributor/conductor back plate, with a preferred range of $2\times$ to $1000\times$ or more. The actual total active surface area of the electrode structure is a function of the properties of the electrode catalyst deposited on the physical electrode structure which may be 2 to 1000 times higher in surface area than the physical electrode base structure.

Cathode **122** may be selected from a number of high surface area materials to include copper, stainless steels, transition metals and their alloys, carbon, and silicon, which may be further coated with a layer of material which may be a conductive metal or semiconductor. The base structure of cathode **122** may be in the form of fibrous, metal foams, reticulated, or sintered powder materials made from metals, carbon, or other conductive materials including polymers. The materials may be a very thin plastic screen incorporated against the cathode side of the membrane to prevent the membrane **120** from directly touching the high surface area cathode structure. The high surface area cathode structure may be mechanically pressed against a cathode current distributor backplate, which may be composed of material that has the same surface composition as the high surface area cathode.

In addition, cathode **122** may be a suitable conductive electrode, such as Al, Au, Ag, Bi, C, Cd, Co, Cr, Cu, Cu alloys (e.g., brass and bronze), Ga, Hg, In, Mo, Nb, Ni, NiCo_2O_4 , Ni alloys (e.g., Ni 625, NiHx), Ni—Fe alloys, Pb, Pd alloys (e.g., PdAg), Pt, Pt alloys (e.g., PtRh), Rh, Sn, Sn alloys (e.g., SnAg, SnPb, SnSb), Ti, V, W, Zn, stainless steel (SS) (e.g., SS 2205, SS 304, SS 316, SS 321), austenitic steel, ferritic steel, duplex steel, martensitic steel, Nichrome (e.g., NiCr 60:16 (with Fe)), Elgiloy (e.g., Co—Ni—Cr), degenerately doped n-Si, degenerately doped n-Si:As, degenerately doped n-Si:B, degenerately doped n-Si, degenerately doped n-Si:As, and degenerately doped n-Si:B. Other conductive electrodes may

be implemented to meet the criteria of a particular application. For photoelectrochemical reductions, cathode **122** may be a p-type semiconductor electrode, such as p-GaAs, p-GaP, p-InN, p-InP, p-CdTe, p-GaInP₂ and p-Si, or an n-type semiconductor, such as n-GaAs, n-GaP, n-InN, n-InP, n-CdTe, n-GaInP₂ and n-Si. Other semiconductor electrodes may be implemented to meet the criteria of a particular application including, but not limited to, CoS, MoS₂, TiB, WS₂, SnS, Ag₂S, CoP₂, Fe₃P, Mn₃P₂, MoP, Ni₂Si, MoSi₂, WSi₂, CoSi₂, Ti₄O₇, SnO₂, GaAs, GaSb, Ge, and CdSe.

The catholyte may include a pH range from 1 to 12, preferably from pH 4 to pH 10. The selected operating pH may be a function of any catalysts utilized in operation of the electrochemical cell **102**. Preferably, catholyte and catalysts may be selected to prevent corrosion at the electrochemical cell **102**. The catholyte may include homogeneous catalysts. Homogeneous catalysts are defined as aromatic heterocyclic amines and may include, but are not limited to, unsubstituted and substituted pyridines and imidazoles. Substituted pyridines and imidazoles may include, but are not limited to mono and disubstituted pyridines and imidazoles. For example, suitable catalysts may include straight chain or branched chain lower alkyl (e.g., C1-C10) mono and disubstituted compounds such as 2-methylpyridine, 4-tertbutyl pyridine, 2,6 dimethylpyridine (2,6-lutidine); bipyridines, such as 4,4'-bipyridine; amino-substituted pyridines, such as 4-dimethylamino pyridine; and hydroxyl-substituted pyridines (e.g., 4-hydroxy-pyridine) and substituted or unsubstituted quinoline or isoquinolines. The catalysts may also suitably include substituted or unsubstituted dinitrogen heterocyclic amines, such as pyrazine, pyridazine and pyrimidine. Other catalysts generally include azoles, imidazoles, indoles, oxazoles, thiazoles, substituted species and complex multi-ring amines such as adenine, pterine, pteridine, benzimidazole, phenanthroline and the like.

The catholyte may include an electrolyte. Catholyte electrolytes may include alkali metal bicarbonates, carbonates, sulfates, phosphates, borates, and hydroxides. Non-aqueous electrolytes, such as propylene carbonate, methanesulfonic acid, methanol, and other ionic conducting liquids may be used rather than water and using salt addition electrolytes such as alkali metal salts. The electrolyte may comprise one or more of Na₂SO₄, KCl, NaNO₃, NaCl, NaF, NaClO₄, KClO₄, K₂SiO₃, CaCl₂, a guanidinium cation, a H cation, an alkali metal cation, an ammonium cation, an alkylammonium cation, a tetraalkyl ammonium cation, a halide anion, an alkyl amine, a borate, a carbonate, a guanidinium derivative, a nitrite, a nitrate, a phosphate, a polyphosphate, a perchlorate, a silicate, a sulfate, and a hydroxide.

The catholyte may further include an aqueous or non-aqueous solvent. An aqueous solvent may include greater than 5% water. A non-aqueous solvent may include as much as 5% water. A solvent may contain one or more of water, a protic solvent, or an aprotic polar solvent. Representative solvents include methanol, ethanol, acetonitrile, propylene carbonate, ethylene carbonate, dimethyl carbonate, diethyl carbonate, dimethylsulfoxide, dimethylformamide, acetonitrile, acetone, tetrahydrofuran, N,N-dimethylacetamide, dimethoxyethane, diethylene glycol dimethyl ester, butyrolonitrile, 1,2-difluorobenzene, γ -butyrolactone, N-methyl-2-pyrrolidone, sulfolane, 1,4-dioxane, nitrobenzene, nitromethane, acetic anhydride, ionic liquids, and mixtures thereof.

In one embodiment, a catholyte/anolyte flowrate may include a catholyte/anolyte cross sectional area flow rate range such as 2-3,000 gpm/ft² or more (0.0076-11.36 m³/m²). A flow velocity range may be 0.002 to 20 ft/sec (0.0006 to 6.1

m/sec). Operation of the electrochemical cell catholyte at a higher operating pressure allows more dissolved carbon dioxide to dissolve in the aqueous solution. Typically, electrochemical cells can operate at pressures up to about 20 to 30 psig in multi-cell stack designs, although with modifications, the electrochemical cells may operate at up to 100 psig. The electrochemical cell may operate the anolyte and the catholyte at the same pressure range to minimize the pressure differential on a separator **120** or membrane separating the two regions. Special electrochemical designs may be employed to operate electrochemical units at higher operating pressures up to about 60 to 100 atmospheres or greater, which is in the liquid CO₂ and supercritical CO₂ operating range.

In another embodiment, a portion of a catholyte recycle stream may be separately pressurized using a flow restriction with backpressure or using a pump, with CO₂ injection, such that the pressurized stream is then injected into the catholyte region of the electrochemical cell which may increase the amount of dissolved CO₂ in the aqueous solution to improve the conversion yield. In addition, microbubble generation of carbon dioxide can be conducted by various means in the catholyte recycle stream to maximize carbon dioxide solubility in the solution.

Catholyte may be operated at a temperature range of -10 to 95° C., more preferably 5-60° C. The lower temperature will be limited by the catholytes used and their freezing points. In general, the lower the temperature, the higher the solubility of CO₂ in an aqueous solution phase of the catholyte, which would help in obtaining higher conversion and current efficiencies. The drawback is that the operating electrochemical cell voltages may be higher, so there is an optimization that would be done to produce the chemicals at the lowest operating cost. In addition, the catholyte may require cooling, so an external heat exchanger may be employed, flowing a portion, or all, of the catholyte through the heat exchanger and using cooling water to remove the heat and control the catholyte temperature.

Anolyte operating temperatures may be in the same ranges as the ranges for the catholyte, and may be in a range of 0° C. to 95° C. In addition, the anolyte may require cooling, so an external heat exchanger may be employed, flowing a portion, or all, of the anolyte through the heat exchanger and using cooling water to remove the heat and control the anolyte temperature.

Electrochemical cells may include various types of designs. These designs may include zero gap designs with a finite or zero gap between the electrodes and membrane, flow-by and flow-through designs with a recirculating catholyte electrolyte utilizing various high surface area cathode materials. The electrochemical cell may include flooded co-current and counter-current packed and trickle bed designs with the various high surface area cathode materials. Also, bipolar stack cell designs and high pressure cell designs may also be employed for the electrochemical cells.

Anode electrodes may be the same as cathode electrodes or different. For sulfur dioxide and hydrogen sulfide anode oxidation chemistry under acid conditions, the preferred electrocatalytic coatings may include precious metal oxides such as ruthenium and iridium oxides, as well as platinum and gold and their combinations as metals and oxides on valve metal substrates such as titanium, tantalum, zirconium, or niobium. Carbon and graphite may also be suitable for use as anodes in addition to boron-doped diamond films on metal or other electrically conductive substrates. For other sulfur based reactants in the anolyte such as sodium sulfide or hydrogen sulfide being oxidized under alkaline conditions, such as in a

13

hydroxide containing electrolyte, selected anode materials may include carbon, transition metals, transitional metal oxides carbon steel, stainless steels, and their alloys and combinations which are stable as anodes. Anode 124 may include electrocatalytic coatings applied to the surfaces of the base anode structure. Anolytes may be the same as catholytes or different. The anolyte electrolytes may be the same as catholyte electrolytes or different. The anolyte may comprise solvent. The anolyte solvent may be the same as catholyte solvent or different. For example, for acid anolytes containing SO_2 as the sulfur-based reactant, the preferred electrocatalytic coatings may include precious metal oxides such as ruthenium and iridium oxides, as well as platinum and gold and their combinations as metals and oxides on valve metal substrates such as titanium, tantalum, zirconium, or niobium. For other anolytes, comprising alkaline or hydroxide electrolytes, anodes may include carbon, cobalt oxides, stainless steels, transition metals, and their alloys, oxides, and combinations. High surface area anode structures that may be used which would help promote the reactions at the anode. The high surface area anode base material may be in a reticulated form composed of fibers, sintered powder, sintered screens, and the like, and may be sintered, welded, or mechanically connected to a current distributor back plate that is commonly used in bipolar cell assemblies. In addition, the high surface area reticulated anode structure may also contain areas where additional applied catalysts on and near the electrocatalytic active surfaces of the anode surface structure to enhance and promote reactions that may occur in the bulk solution away from the anode surface such as the introduction of SO_2 into the anolyte. The anode structure may be graded, so that the suitable of the may vary in the vertical or horizontal direction to allow the easier escape of gases from the anode structure. In this gradation, there may be a distribution of particles of materials mixed in the anode structure that may contain catalysts, such as transition metal based oxides, such as those based on the transition metals such as Co, Ni, Mn, Zn, Cu and Fe as well as precious metals and their oxides based on platinum, gold, silver and palladium which may be deposited on inorganic supports within cathode compartment space 118 or externally, such as in the second product extractor or a separate reactor.

Separator 120, also referred to as a membrane, between a first region 118 and second region 118, may include cation ion exchange type membranes. Cation ion exchange membranes which have a high rejection efficiency to anions may be preferred. Examples of such cation ion exchange membranes may include perfluorinated sulfonic acid based ion exchange membranes such as DuPont Nafion® brand unreinforced types N117 and N120 series, more preferred PTFE fiber reinforced N324 and N424 types, and similar related membranes manufactured by Japanese companies under the supplier trade names such as AGC Engineering (Asahi Glass) under their tradename Flemion®. Other multi-layer perfluorinated ion exchange membranes used in the chlor alkali industry may have a bilayer construction of a sulfonic acid based membrane layer bonded to a carboxylic acid based membrane layer, which efficiently operates with an anolyte and catholyte above a pH of about 2 or higher. These membranes may have a higher anion rejection efficiency. These are sold by DuPont under their Nafion® trademark as the N900 series, such as the N90209, N966, N982, and the 2000 series, such as the N2010, N2020, and N2030 and all of their types and subtypes. Hydrocarbon based membranes, which are made from of various cation ion exchange materials can also be used if a lower the anion rejection efficiency is not as important, such as those sold by Sybron under their trade

14

name Ionac®, AGC Engineering (Asahi Glass) under their trade name under their Selemion® trade name, and Tokuyama Soda, among others on the market. Ceramic based membranes may also be employed, including those that are called under the general name of NASICON (for sodium super-ionic conductors) which are chemically stable over a wide pH range for various chemicals and selectively transports sodium ions, the composition is $\text{Na}_1+x\text{Zr}_2\text{Si}_x\text{P}_3-x\text{O}_{12}$, and well as other ceramic based conductive membranes based on titanium oxides, zirconium oxides and yttrium oxides, and beta aluminum oxides. Alternative membranes that may be used are those with different structural backbones such as polyphosphazene and sulfonated polyphosphazene membranes in addition to crown ether based membranes. Preferably, the membrane or separator is chemically resistant to the anolyte and catholyte.

A rate of the generation of reactant formed in the anolyte compartment from the anode reaction, such as the oxidation of sulfur dioxide to sulfur trioxide, is contemplated to be proportional to the applied current to the electrochemical cell 102. The rate of the input or feed of the sulfur-based reactant, for example sulfur dioxide, into the second region 118 should then be fed in proportion to the generated reactant. The molar ratio of the sulfur-based reactant to the generated anode reactant may be in the range of 100:1 to 1:10, and more preferably in the range of 50:1 to 1:5. The anolyte product output in this range may contain unreacted sulfur-based reactant. The operation of the extractor 112 and its selected separation method, for example fractional distillation or packed tower scrubbing, the actual products produced, and the selectivity of the wanted reaction would determine the optimum molar ratio of the sulfur-based reactant to the generated reactant in the anode compartment. Any of the unreacted components would be recycled to the second region 118.

Similarly, a rate of the generation of the formed electrochemical carbon dioxide reduction product, is contemplated to be proportional to the applied current to the electrochemical cell 102. The rate of the input or feed of the carbon dioxide source 106 into the first region 116 should be fed in a proportion to the applied current. The cathode reaction efficiency would determine the maximum theoretical formation in moles of the carbon dioxide reduction product. It is contemplated that the ratio of carbon dioxide feed to the theoretical moles of potentially formed carbon dioxide reduction product would be in a range of 100:1 to 2:1, and preferably in the range of 50:1 to 5:1, where the carbon dioxide is in excess of the theoretical required for the cathode reaction. The carbon dioxide excess would then be separated in the extractor 110 and recycled back to the first region 116.

The electrochemical cell can be easily operated at a current density of greater than 3 kA/m^2 (300 mA/cm^2), or in suitable range of 0.5 to 5 kA/m^2 or higher if needed. The anode preferably has a high surface area structure with a specific surface area of $50 \text{ cm}^2/\text{cm}^3$ or more that fills the gap between the cathode backplate and the membrane, thus having a zero gap anode configuration. Metal and/or metal oxide catalysts may be added to the anode in order to decrease anode potential and/or increase anode current density. Stainless steels or nickel may also be used as anode materials with for sodium sulfide oxidation under alkaline conditions. For sulfur dioxide and hydrogen sulfide gas reactions at the anode, under acidic conditions, anodes with precious metal oxide coatings on valve metal substrates are the preferred materials, but others may also be suitable.

In the present disclosure, the methods disclosed may be implemented as sets of instructions or software readable by a device. Further, it is understood that the specific order or

15

hierarchy of steps in the methods disclosed are examples of exemplary approaches. Based upon design preferences, it is understood that the specific order or hierarchy of steps in the method can be rearranged while remaining within the disclosed subject matter. The accompanying method claims present elements of the various steps in a sample order, and are not necessarily meant to be limited to the specific order or hierarchy presented.

It is believed that the present disclosure and many of its attendant advantages will be understood by the foregoing description, and it will be apparent that various changes may be made in the form, construction and arrangement of the components without departing from the disclosed subject matter or without sacrificing all of its material advantages. The form described is merely explanatory, and it is the intention of the following claims to encompass and include such changes.

What is claimed is:

1. A method for producing a first product from a first region of an electrochemical cell having a cathode and a second product from a second region of the electrochemical cell having an anode, the method comprising the steps of:

contacting the first region with a catholyte comprising carbon dioxide;

contacting the second region with an anolyte comprising a sulfur-based reactant and a nitrogen-based reactant;

applying an electrical potential between the anode and the cathode sufficient to reduce carbon dioxide at the cathode to produce a first product recoverable from the first region and a second product recoverable from the second region;

removing the second product, an unreacted sulfur-based reactant and an unreacted nitrogen-based reactant from the second region;

recycling the unreacted sulfur-based reactant and the unreacted nitrogen-based reactant to the second region;

removing the first product from the first region;

reacting the first product with water to produce carbon dioxide; and

recycling the carbon dioxide to the first region.

2. The method according to claim 1, wherein the sulfur-based reactant includes at least one of sulfur dioxide, hydrogen sulfide, an alkali metal sulfide, an alkali metal sulfite, bisulfite, or thiosulfate.

3. The method according to claim 1, wherein the second product includes at least one of sulfur trioxide, sulfuric acid, alkali metal sulfites, alkali metal thiosulfates, or alkali metal polysulfides.

4. The method according to claim 1, wherein the first product includes carbon monoxide.

5. The method according to claim 1, further comprising: converting the second product to a third product.

6. The method according to claim 1, wherein the anolyte and the catholyte are non-aqueous.

7. The method according to claim 6, wherein the second product comprises at least one of sodium sulfite and sodium thiosulfate.

8. The method according to claim 1, wherein the sulfur-based reactant is sulfur dioxide and the second product is sulfur trioxide.

9. The method according to claim 8, further comprising: converting the second product to sulfuric acid.

10. The method according to claim 1, wherein the catholyte further comprises at least one of sodium bicarbonate or potassium bicarbonate.

11. The method according to claim 1, wherein the catholyte is liquid phase and the anolyte is gas phase.

16

12. The method according to claim 1, wherein the cathode and the anode are separated by an ion permeable barrier that operates at a temperature less than 600 degrees C and the ion permeable barrier includes one of a polymeric or inorganic ceramic-based ion permeable barrier.

13. The method according to claim 1, wherein the nitrogen-based reactant includes at least one of nitric oxide, nitrogen dioxide, nitrous oxide, ammonia, an alkali metal nitrite, or an alkali metal nitrate.

14. The method according to claim 1, wherein the second product includes nitric acid.

15. The method according to claim 1, wherein the second product includes nitric acid and at least one of sulfur trioxide, sulfuric acid, alkali metal sulfites, alkali metal thiosulfates, or alkali metal polysulfides.

16. A method for producing a first product from a first region of an electrochemical cell having a cathode and a second product from a second region of the electrochemical cell having an anode, the method comprising the steps of:

receiving a feed of carbon dioxide at the first region of the electrochemical cell;

contacting the first region with a catholyte comprising carbon dioxide;

receiving a feed of a sulfur-based reactant and a nitrogen-based reactant at the second region of the electrochemical cell;

contacting the second region with an anolyte comprising the sulfur-based reactant and a nitrogen-based reactant;

applying an electrical potential between the anode and the cathode sufficient to reduce carbon dioxide at the cathode to produce a first product recoverable from the first region and a second product recoverable from the second region;

removing the second product, an unreacted sulfur-based reactant and an unreacted nitrogen-based reactant from the second region;

recycling the unreacted sulfur-based reactant and the unreacted nitrogen-based reactant to the second region;

removing the first product from the first region;

reacting the first product with water to produce carbon dioxide; and

recycling the carbon dioxide to the first region.

17. The method according to claim 16, wherein the sulfur-based reactant includes at least one of sulfur dioxide, sodium sulfide, hydrogen sulfide, an alkali metal sulfide, an alkali metal sulfite, bisulfite, or thiosulfate.

18. The method according to claim 16, wherein the second product includes at least one of sulfur trioxide, sodium sulfite, sodium thiosulfate or sodium polysulfide.

19. The method according to claim 16, wherein the first product includes carbon monoxide.

20. The method according to claim 16, wherein the sulfur-based reactant is sulfur dioxide and the second product is sulfur trioxide.

21. The method according to claim 20, further comprising: converting the sulfur trioxide to sulfuric acid.

22. The method according to claim 16, wherein the catholyte is liquid phase and the anolyte is gas phase.

23. The method according to claim 16, wherein the cathode and the anode are separated by an ion permeable barrier; wherein the ion permeable barrier includes one of a polymeric or inorganic ceramic-based ion permeable barrier; wherein the barrier operates at a temperature less than 600 degrees C.

24. A system for electrochemical co-production of products, comprising:

17

an electrochemical cell including:

- a first region;
- a cathode associated with the first region;
- a second region;
- an anode associated with the second region; and
- a separator for selectively controlling a flow of ions between the first region and the second region;
- a carbon dioxide source, the carbon dioxide source in flow communication with the first region to supply carbon dioxide to the first region;
- a sulfur-based reactant source, the sulfur-based reactant source in flow communication with the second region to supply a sulfur-based reactant to said second region;
- a nitrogen-based reactant source, the nitrogen-based reactant source in flow communication with the second region to supply a nitrogen-based reactant to said second region;
- an energy source for applying a current across the anode and the cathode, wherein when current is applied, a first product recoverable from the first region and a second product is recoverable from the second region; and
- a reactor for reacting the first product recoverable from the first region with water to produce carbon dioxide that is recycled to the first region.

25. The system according to claim **24**, wherein the recycled sulfur-based reactant includes at least one of sulfur dioxide, sodium sulfide, hydrogen sulfide, an alkali metal sulfide, an alkali metal sulfite, bisulfite, or thiosulfate.

26. The system according to claim **24**, wherein the second product includes at least one of sulfur trioxide, sodium sulfite, or sodium thiosulfate.

27. The system according to claim **24**, wherein the first product includes carbon monoxide.

28. The system according to claim **24**, wherein the sulfur-based reactant is sulfur dioxide and the second product is sulfur trioxide.

18

29. The system according to claim **24**, wherein the separator includes an ion permeable barrier and selectively controls a flow of ions between the first region and the second region at a temperature less than 600 degrees C.

30. A method for producing a first product from a first region of an electrochemical cell having a cathode and a second product from a second region of the electrochemical cell having an anode, the method comprising the steps of:

- contacting the first region with a catholyte, the catholyte consisting essentially of carbon dioxide, solvent, a catalyst and an electrolyte;
- contacting the second region with an anolyte comprising a nitrogen-based reactant;
- applying an electrical potential between the anode and the cathode sufficient to produce a first product recoverable from the first region and a second product recoverable from the second region;
- removing the second product and an unreacted nitrogen-based reactant from the second region;
- recycling the unreacted nitrogen-based reactant to the second region.
- removing the first product from the first region;
- reacting the first product with water to produce carbon dioxide; and
- recycling the carbon dioxide to the first region.

31. The method according to claim **30**, wherein the nitrogen-based reactant includes at least one of nitric oxide, nitrogen dioxide, nitrous oxide, ammonia, an alkali metal nitrite, or an alkali metal nitrate.

32. The method according to claim **30**, wherein the second product includes nitric acid.

33. The method according to claim **30**, wherein the cathode and the anode are separated by an ion permeable barrier that operates at a temperature less than 600 degrees C. and the ion permeable barrier includes one of a polymeric or inorganic ceramic-based ion permeable barrier.

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